

CHARACTERIZATION OF COAL MACERALS ON THE BASIS OF THEIR FLUORESCENT SPECTRA

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INTRODUCTION

One of the major problems of coal science is that very little is known about the basic properties of the various macerals that make up coal. Two of the main reasons for this lack of knowledge about the properties of coal macerals is that they are extremely difficult to separate from coal and that they are non-crystalline organic compounds and, therefore, not good subjects to analyze with such standard methods as x-ray diffraction or electron-microprobe analysis. Some of the most successful characterization of coal macerals to date has been by petrographic methods, in which the individual macerals do not have to be separated. In the steel industry, for example, petrographic techniques have proven so successful in allowing the prediction of the coking properties of coal that most major steel companies have now established petrographic laboratories. Another petrographic technique that has only recently been applied to coal analysis is qualitative and quantitative fluorescence microscopy. With this technique, the visible fluorescent light excited from the macerals reveals shapes, textures and colors not visible in normal white-light viewing. The technique also yields quantitative spectra that are characteristic of both the individual maceral type and the rank of the coal. It is now also well established that all of the liptinite macerals (derived from the resinous and waxy parts of plants) and some of the vitrinite macerals will fluoresce, and that some recently discovered liptinite macerals can only be identified by their fluorescence properties. Some of the first measurements of the absolute intensity of fluorescence of coal macerals at specific wavelengths were made by Jacob (1,2). Relative intensity measurements of fluorescent spectra of modern plant materials, peats and coals have been reported by van Gijzel (3,4,5). Teichmüller (6,7,8) described three new members of the liptinite group of macerals in part by demonstrating their distinctive spectral properties. Ottenjann, Teichmüller and Wolf (9) illustrated the correlation of changes in fluorescence spectra of sporinite with rank, and Crelling and others (10) and Crelling (11) have demonstrated the use of fluorescence spectra to discriminate macerals. In addition, Ottenjann, Wolf, and Wolff-Fischer (12) have been able to relate the fluorescence spectra of vitrinite macerals to the technological properties of coal. These studies have shown the potential of using fluorescence measurements in the study of liptinite and vitrinite macerals.

EQUIPMENT AND METHODS

The fluorescence microscopy system used in the SIUC Coal Characterization Laboratory is a Leitz MPV II reflectance microscope which is fitted with a 100 watt mercury arc lamp, a Ploem illuminator and a Leitz oil immersion 40X objective with a 1.3 numerical aperture. For spectral measurements the light from the mercury arc passes through a UG1 ultra-violet filter to a TK400 dichroic mirror which reflects light less than 400 nm to the sample. The fluorescent light excited from the sample is passed through a 430 nm barrier filter to a motorized interference wedge in front of the photometer. The interference wedge controls the wavelength of the fluorescent light hitting the photometer so that the intensity variations from 430 to 700 nm can be scanned and recorded in about 40 seconds.

The spectral data are then fed into a computer from the microscope system and digitized, corrected and analyzed. Each spectrum is corrected for the effects of background fluorescence and for the effects of the microscope system, especially the sensitivity of the photo-multiplier tube, following correction procedures described by van Gijzel (13). For comparison the various spectra are normalized and reduced to a number of parameters such as: 1) the wavelength of maximum intensity peak (λ_{max}); 2) the red/green quotient (Q) where Q = relative intensity at 650 nm/relative intensity at 500 nm; 3) the area below λ_{max} ; 4) the area above λ_{max} ; 5) area blue (430 to 500 nm); 6) area green (500 to 570 nm); 7) area yellow (570 to 630 nm); and 8) area red (630 to 700 nm).

RESULTS AND DISCUSSION

In coals of the Illinois Basin, standard white-light petrographic methods generally reveal three types of liptinite macerals, resinite, sporinite and cutinite. These macerals are identified on the basis of their petrographic properties such as reflectance, size, shape and texture. When qualitative fluorescence analysis is used, the fluorescence colors and intensity commonly reveal an additional maceral, fluorinite. When fluorescence spectral analysis is used, the spectral data distinguish these four types of liptinite macerals plus additional varieties of resinite, sporinite and cutinite. Also, altered or weathered varieties of these macerals can be distinguished in some coals. For example, spectral analysis of the various liptinite macerals in samples of the Herrin (No. 6) coal seam with a reflectance of 0.65% (in oil at 546 nm) showed distinctive spectra for the macerals fluorinite, resinite, sporinite and cutinite. In this case, the spectra were assigned to maceral groups on the basis of the petrographic identification of macerals from which the spectra were obtained. When the groups of spectral data for each maceral type were subjected to discriminant function analysis of the eight different parameters for each spectrum, the maceral types were well separated. From this analysis it was easily seen that there were two different groups of resinite macerals. Thus, the statistical analysis of the spectral parameters of the macerals revealed two varieties of the resinite maceral group that could not be readily distinguished by normal petrographic means. The average spectra of the various maceral types distinguished by the discriminant function analysis are plotted in Figure 1. The combined results of maceral analyses in both white-light and fluorescent light as well as the reflectance value for the Herrin (No. 6) coal are given in Table 1.

Table 1.

RESULTS OF COMBINED WHITE-LIGHT AND FLUORESCENT LIGHT PETROGRAPHIC ANALYSES

<u>Coal Seam</u>	<u>Herrin (No. 6)</u>	<u>Brazil Block</u>	<u>Hiawatha</u>
Reflectance (in oil at 546 nm)	0.65	0.58	0.52
Vitrinite	65.1	56.3	73.7
Pseudovitrinite	19.8	8.7	7.8
Fluorinite	0.3	0.2	0
Resinite	0.1	0.7	6.9
Sporinite	3.0	14.1	0.5
Cutinite	0.4	2.0	0.8
Amorphous Liptinite	1.8	4.2	1.0
Semi-fusinite	5.7	4.9	4.2
Fusinite	2.1	3.4	1.3
Micrinite	1.7	5.5	3.8

In a study on the fluorescence properties of the Brazil Block seam, a somewhat different approach was used. In this case, about a hundred individual spectra were taken on all fluorescing liptinite macerals. Although the macerals from which the spectra were taken were not identified at that time, photomicrographs in both normal white-light and fluorescent light were taken for documentation. The spectral parameters for each spectrum were calculated and these data were subjected to cluster analysis to generate groupings of spectra on the basis of the spectral parameters. When these groups were identified they were subjected to discriminant function analysis to test degree to which the groups could be separated on the basis of their spectral parameters. It was found that seven groups could be distinguished. The basic petrographic data for the Brazil Block coal seam are given in Table 1 and the average spectral parameters for each group are given in Table 2. When the macerals from which the spectra were taken were identified from the photomicrographs, it was found that each group corresponded to a separate maceral type or a variety of a maceral type. There was one type of fluorinite, one type of resinite, three types of sporinite and two types of cutinite. While this correspondence of maceral types and varieties to statistical groupings of spectral data was not unexpected, it is further confirmation that the spectral parameters of macerals are unique to maceral type and variety.

Table 2.

SPECTRAL PARAMETERS OF AVERAGE SPECTRA
OF THE BRAZIL BLOCK COAL SEAM

Parameter	Fluorinite	Resinite	Sporinite			Cutinite	
			I	II	III	I	II
Peak (nm)	480	520	550	590	690	610	650
Red/Green Quotient	0.32	0.58	0.85	1.00	1.22	1.47	2.27
Area Blue (%)	37	19	16	14	13	12	7
Area Green (%)	38	43	36	34	31	32	29
Area Yellow (%)	15	23	25	28	26	28	29
Area Red (%)	10	15	23	24	30	28	35
Area Left of Peak (%)	21	33	40	53	93	59	60
Area Right of Peak (%)	79	67	60	47	7	41	40

An interesting result of this analysis is that one of the sporinite varieties and one of the cutinite varieties distinguished by statistical means showed petrographic evidence of alteration (weathering). Because the coal sample itself was collected from a fresh exposure at an active mine, it appears as if the weathered maceral varieties were weathered before they were incorporated into the peat that was later coalified.

The results of these two studies show that fluorescence spectral analysis can distinguish on a quantitative basis the various types of liptinite macerals and, indeed, even varieties of each type. That the various spectra are unique to the individual macerals is further indicated by the recurrent order of the spectral parameters, especially the wavelength of maximum intensity (λ_{max}) and the red/green quotient in any given coal. For example, as shown in Figure 1 for the Herrin (No. 6) seam and in Table 2 for the Brazil Block seam the order of the maceral types on the basis of increasing λ_{max} and Q is fluorinite, resinite, sporinite and cutinite. It should be noted, however, that as the rank of coal increases, all of the spectral peaks shift toward longer wavelengths and diminish in intensity and are thus difficult or impossible to distinguish from each other. Weathering of the macerals has a similar effect.

However, even when macerals have been altered by increases in rank, or weathering, or other processes, fluorescence microscopy can sometimes still be quite useful in characterizing coal macerals. For example, in some coal seams in the western U.S. there is an abundance of resinite. In fact, the resinite is being extracted from some of these coals and commercially exploited as a chemical raw material. In these seams the resinite most often occurs as a secondary material, filling fissures and voids in the coal. Numerous flow textures, inclusions of coal in resinite veinlets, and intrusive relationships throughout coal seams indicate that the resinite was mobilized at some point in its history. These secondary resinites are often difficult to detect in normal white-light viewing, however, they all tend to fluoresce strongly in a variety of colors and are therefore, quite amenable to fluorescence analysis. When samples of the Hiawatha seam from Utah are so examined, four types of secondary resinites, each with a different fluorescence color -- green, yellow, orange, red-brown -- are seen. Each type has a spectra that is distinctive and the various types can also be statistically separated on the basis of their spectral parameters. The average spectra of the four resinite types are shown in Figure 2 and the basic petrographic analysis of the sample from the Hiawatha seam is given in Table 1. It should be noted that at this time the only way to distinguish the various types of secondary resinite is with fluorescence microscopy. Work is now underway to separate these various resinite types and chemically characterize them.

SUMMARY

Although the characterization of coal macerals on the basis of their fluorescence spectral is a recent innovation, it has already proven to be an excellent fingerprinting tool for the various macerals. In some cases, it is even more sensitive than normal petrographic analysis. The initial results of fluorescence spectral studies show that the various fluorescent macerals in single coals can be statistically separated on the basis of their spectral parameters and that even varieties of one type of maceral can be so separated. Although the spectra obtained at this time are rather broad and not suitable for chemical structure analysis, the potential for structural analysis exist and may be realized with improvements in instrumentation.

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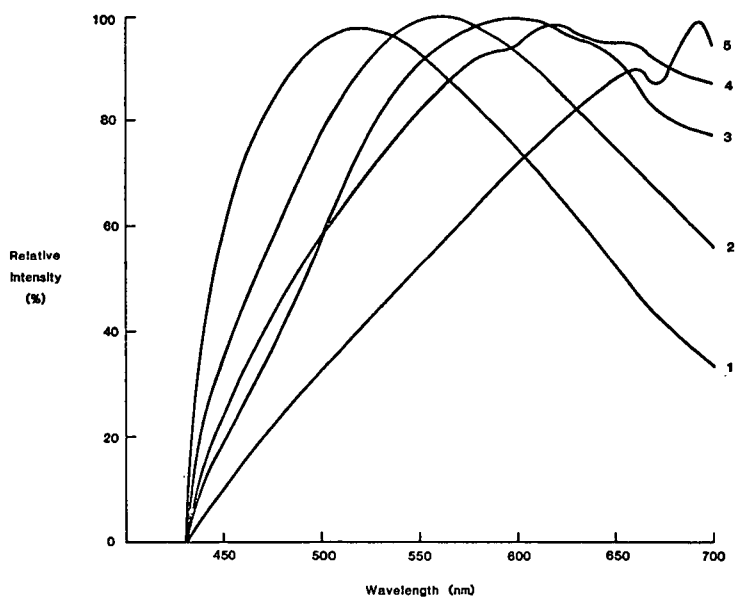


Figure 1. Average fluorescence spectrum for various macerals in the Herrin (No. 6) coal seam: 1) fluorinite; 2) low-peaking resinite; 3) high-peaking resinite; 4) sporinite; 5) cutinite. Vitrinite reflectance of the seam is 0.65%.

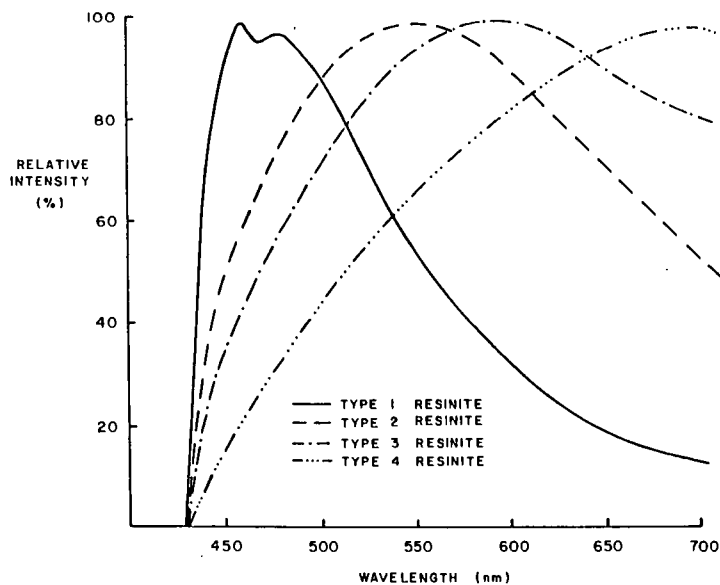


Figure 2. Average fluorescence spectra of resinite macerals in the Hiawatha seam, Utah after Crelling, et al. (10)